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## (54) Transesterification process

(57) A process which enables the production of various monomers is disclosed. Compounds to prevent the unwanted polymerization of monomers and monomer compositions containing those compounds are also disclosed.

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the solution was cooled to 70°C and to it was added 7.9 grams (0.014 moles) of tetraethylhexyl titanate and 83.2 grams (0.83 moles) of MMA. The solution was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 30 - 35 ml. / min. and heated to reflux under reduced pressure (550 mm of Hg) for 4 hours while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 57.6 to 91.2°C and the temperature in the pot was 99 to 106°C. The conversion of E20CSA to E20CSMA was determined to be 94.9 % based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. The MMA was removed in vacuo (pot temperature / pressure of 45 to 109°C / 62 to 45 mm of Hg) from the stirred and 8% O2 - 92% N2 sparged mixture. The stirred mixture was cooled to 45°C and 4.10 grams (0.028 moles) of 2-ethyl hexanediol was added. The mixture was stirred and the solution temperature was maintained at 51 to 53°C for 1 hour. To the mixture was added 125.16 grams (1.454 moles) of glacial methacrylic acid. The mixture was stirred for 35 minutes and to it was added 62.6 grams (3.48 moles) of water. The cloud point of the product, an orange liquid, was 52°C. The cloud point was determined by preparing a solution of product in DI water (weight ratio of 1 part product to 99 parts water) and heating the stirred mixture to the point where the mixture became cloudy. The lowest temperature at which the mixture became cloudy was registered as the cloud point.

Example 6 - Polyethoxy cetyl-stearyl methacrylate with lithium hydroxide catalyst

**[0023]** A mixture of 400.0 grams (0.35 moles) of E20CSA that contained 1,021 ppm of p-methoxy phenol (MEHQ), 250.0 grams (2.5 moles) of methyl methacrylate (MMA), 0.4 grams (0.00323 moles) of MEHQ, and 0.1 grams (0.0006 moles) of 4-hydroxy-2,2,6,6-tetramethylpiperidinyl free radical was added to a 1 liter, 4-necked flask equipped with a thermocouple with temperature readout, mechanical stirrer, 8% $O_2$ - 92% $N_2$ sparge inlet and a 1 inch diameter 10 plate Oldershaw column fitted with a distillation head, distillate rate removal-vapor pressure temperature controller, and a graduated distillate receiver. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 7 to 35 ml. / min. and heated to reflux under reduced pressure (550 mm of Hg) for 0.75 hours while removing the MMA-water azeotrope. During the dehydration stage of the batch the temperature at the top of the column was 65.2 to 85.8°C and the temperature in the pot was 95 to 100° C. At the conclusion of the dehydration of the batch the solution was cooled to 50 to 70°C and to it was added 0.3 grams (0.007 moles) of lithium hydroxide monohydrate and 62.0 grams (0.62 moles) of MMA. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 7 - 35 ml. / min. and heated to reflux under reduced pressure (550 mm of Hg) for 2 hours 40 min. while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 58.0 to 87.1°C and the temperature in the pot was 95 to 106°C. The conversion of E20CSA to E20CSMA was calculated to be 115.3 % based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. The MMA was removed in vacuo (pot temperature / pressure of 55 to 113°C / 120 to 20 mm of Hg) from the stirred and 8% O2 - 92% N2 sparged mixture. The stirred mixture was cooled to 45°C to afford 423.7 grams of neat E20CSMA.

**[0024]** Some of the neat E20CSMA (141.3 grams) was mixed with 60.5 grams of glacial methacrylic acid for approximately 1/2 hr. at 30 to 45°C. The mixture was polish filtered by vacuum filtration to produce the product mixture of E20CSMA - methacrylic acid. The cloud point of the product, a white - tan liquid, was 51.5 °C.

**[0025]** Some of the neat E20CSMA (141.3 grams) was mixed with 40.4 grams of glacial methacrylic acid for approximately 1/2 hr. at 30 to 45°C. The mixture was stirred for approximately 1/2 hr. and to it was added 20.2 grams of water. The mixture was polish filtered by vacuum filtration to produce the product mixture of E20CSMA - methacrylic acid - water. The cloud point of the product, a white - tan liquid, was 52 to 52.5°C.

**[0026]** For Example 5, the conversion of E20CSA to E20CSMA was 94.9 %. For Example 6, the conversion of E20CSA to E20CSMA was 115.3 %. This data demonstrates that the lithium catalyst is more effective than the titanate catalyst in a transesterification reaction.

Example 7 - Polyethoxy lauryl - myristyl methacrylate

**[0027]** A mixture of 410.9 grams (0.35 moles) of E23LMA that contained 954 ppm of MEHQ, 213.5 grams (2.135 moles) of MMA, 0.1 grams (0.0011 moles) of DEHA and 0.41 grams (0.0033 moles) of MEHQ was added to a reactor set up as described in Example 1. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ and heated to reflux under reduced pressure (550 mm of Hg) for 40 minutes while removing the MMA-water azeotrope. During the dehydration stage of the batch the temperature at the top of the column was 83 to 92°C and the temperature in the pot was 105 to 111°C. At the conclusion of the dehydration of the batch the solution was cooled to 70°C and to it was added 2.38 grams (0.007 moles) of tetrabutyl titanate and 53 grams (0.53 moles) of MMA. The solution was stirred, sparged with 8% $O_2$ - 92% $N_2$ and heated to reflux under reduced pressure (550 mm of Hg) for 3.25 hours while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-

methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 57.7 to 59.6°C and the temperature in the pot was 104 to 114°C. The conversion of E23LMA to E23LMMA was determined to be 99 % based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. The MMA was removed in vacuo (pot temperature / pressure of 47 to 108°C / 70 to 43 mm of Hg) from the stirred and 8% 02 - 92% N2 sparged mixture. The stirred mixture was cooled to 46°C and 1.02 grams (0.007 moles) of 2-ethyl hexanediol was added. The mixture was stirred and the solution temperature was maintained at 50 to 55°C for 1 hour. To the mixture was added 186.3 grams (2.16 moles) of glacial methacrylic acid and the product (627.7 grams), an orange liquid, had a cloud point of 54.4°C. The cloud point was determined by preparing a solution of product in DI water (weight ratio of 1 part product to 99 parts water) and heating the stirred mixture to the point where the mixture became cloudy. The lowest temperature at which the mixture became cloudy was registered as the cloud point.

Example 8 - MEEU / MMA

**[0028]** A mixture of 130.0 grams (1.0 mole) of HEEU, 563.6 grams (5.64 moles) of MMA, 0.25 grams (0.002 moles) of MEHQ, 0.5 grams (0.003 moles) of PTZ and 1.3 grams (0.0146 moles) of DEHA was added to a reactor set up as described in Example 1. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 4 ml. / min. and heated to reflux under reduced pressure (700 mm of Hg) for 50 minutes while removing the MMA-water azeotrope. During the dehydration stage of the batch the temperature at the top of the column was 90 to 98.2°C and the temperature in the pot was 100 to 101°C. At the conclusion of the dehydration of the batch the solution was cooled to 70°C and to it was added 4.18 grams (0.0168 moles) of dibutyl tin oxide, 0.3 grams (0.0034 moles) of DEHA and 100.2 grams (1.0 moles) of MMA. The mixture was stirred, sparged with 8% $O_2$-92% $N_2$ at a rate of 4 ml. / min. and heated to reflux under reduced pressure (700 mm of Hg) for 4 hours 38 minutes while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 64.4 to 97.6°C and the temperature in the pot was 100 to 104°C. The conversion of HEEU to MEEU was determined to be 95.0 % based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. According to HPLC, the product, an orange liquid, contained 27.2 weight % MEEU, 69.4 weight % MMA, 0.35 weight % HEEU, and 1.99 weight % MEMEU.

Example 9 - MEEU / MMA

**[0029]** A mixture of 260.3 grams (2.0 mole) of HEEU, 1,123.8 grams (11.24 moles) of MMA and 0.398 grams (0.0023 moles) of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl free radical was added to a reactor set up as described in Example 5. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 6 to 7 ml. / min. and heated to reflux under reduced pressure (700 mm of Hg) for 25 minutes while removing the MMA-water azeotrope. During the dehydration stage of the batch the temperature at the top of the column was 89.8 to 99°C and the temperature in the pot was 100°C. At the conclusion of the dehydration of the batch the solution was cooled to 70°C and to it was added 8.32 grams (0.0335 moles) of dibutyl tin oxide and 93.0 grams (1.0 moles) of MMA. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 4 - 10 ml. / min. and heated to reflux under reduced pressure (700 mm of Hg) for 3 hours 38 minutes while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 63.4 to 98.7°C and the temperature in the pot was 100 to 104°C. The conversion of HEEU to MEEU was determined to be 96.7% based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. According to ,HPLC the product, an orange liquid, contained 28.7 weight % MEEU, 68.0 weight % MMA, 0.45 weight % HEEU, and 0.8 weight % MEMEU.

Example 10 - DCPOEM

**[0030]** A mixture of 194.0 grams (1.0 mole) of DCPOEA, 120.0 grams (1.2 moles) of MMA, 0.051 grams (0.0004 moles) of MEHQ and 0.049 grams (0.0003 moles) of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl free radical was added to a 500 milliliter 4 necked flask equipped with a thermometer, mechanical stirrer, 8% O2 - 92% N2 sparge inlet and a 1 inch diameter - 10 plate Oldershaw column fitted with a distillation head, distillate rate removal-vapor pressure temperature controller, and a graduated distillate receiver. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ at a rate of 8 - 10 ml. / min. and heated to reflux under reduced pressure (400 mm of Hg) for 13 minutes while removing the MMA-water azeotrope. The temperature at the top of the column was 79.3 to 81.4°C and the temperature in the pot was 99 - 103°C. At the conclusion of the dehydration of the batch the solution was cooled to 70°C and to it was added 3.96 grams (0.007 moles) of tetraethylhexyl titanate and 25.0 grams (0.25 moles) of MMA. The mixture was stirred,

sparged with 8% $O_2$ - 92% $N_2$ at a rate of 4 - 7.5 ml. / min. and heated to reflux under reduced pressure (400 mm of Hg) for 9 hours. During the reaction stage the addition of MMA was made to the batch to help control batch temperature and maintain efficient column operation. The amount of the MMA charges and the elapsed reaction time were: 50 grams (0.5 moles) of MMA added after 2 1/2 hours of reaction time, followed by % hours. of reaction time, followed by the addition of 51 grams (0.51 moles) of MMA and the reaction continuation for 4 1/2 hours. while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. The temperature at the top of the column was 49.2 to 81.1°C and the temperature in the pot was 99 to 115°C. The conversion of the DCPOEA to DCPOEM was estimated to be 95% based on the methanol of reaction - MMA azeotrope removal and its analysis by refractive index. The MMA was removed in vacuo (pot temperature / pressure of 22 to 88°C / 50 to 20 mm of Hg) from the stirred and 8% O2 - 92% N2 sparged mixture. The resulting product was isolated (266.1 grams) and analyzed. GLC analysis showed 95.5 area % DCPOEM, 0.63 area % DCPOEA, 0.46 area % MMA and 1.84 area % ethyl hexyl methacrylate (catalyst byproduct).

Example 11 - DCPOEM - distilled grade

**[0031]** A mixture of 291.0 grams (1.5 mole) of DCPOEA, 238.5 grams (2.39 moles) of MMA, 0.074 grams (0.0006 moles) of MEHQ and 0.074 grams (0.00043 moles) of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl free radical was added to a reactor set up as described in Example 1. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ and heated to reflux under reduced pressure (400 mm of Hg) for 16 minutes while removing the MMA-water azeotrope. The temperature at the top of the column was 79.9 to 82.6°C and the temperature in the pot was 96 - 103°C. At the conclusion of the dehydration of the batch the solution was cooled to 70°C and to it was added 5.93 grams (0.0105 moles) of tetraethylhexyl titanate and 10.0 grams (0.1 moles) of MMA. The mixture was stirred, sparged with 8% $O_2$ - 92% $N_2$ and heated to reflux under reduced pressure (400 mm of Hg) for 5 hrs. During the reaction stage the addition of MMA was made to the batch to help control batch temperature and maintain efficient column operation. The amount of the MMA charges and the elapsed reaction time were:
56.8 grams (0.568 moles) of MMA added after 2 hrs. of reaction time, followed by 1 hr. of reaction time, followed by the addition of 25.4 grams (0.254 moles) of MMA and 1 hr. of reaction time, followed by the addition of 48.3 grams (0.483 moles) of MMA and the reaction continuation for 1 hr. while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. The temperature at the top of the column was 49.1 to 82.2°C and the temperature in the pot was 100 to 119°C. The conversion of the DCPOEA to DCPOEM was estimated to be 98% based on the methanol of reaction - MMA azeotrope removal and its analysis by refractive index. A mixture of 0.073 grams (0.00043 moles) of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl free radical and the reaction mixture was fractionally vacuum distilled. The major fraction (290.8 grams), a colorless clear liquid, was obtained during the distillation (vapor temperature range/ pot temperature range / pressure of 126 to 135°C / 154 - 160°C / 1. mm of Hg.). Earlier distillation fractions (73.44 grams) contained 62 - 93.6 area % DCPOEM by GLC analysis and the still bottoms (33.05 grams) was not analyzed. GLC analysis showed that the major fraction contained 96.9 area % DCPOEM, < 0.1 area % DCPOEA, < 0.1 area % MMA and < 0.1 area % ethyl hexyl methacrylate (catalyst byproduct).

Example 12 - Oxazolidinylethyl Methacrylate - Continuous Process

**[0032]** MMA containing 2,000 ppm PTZ and 200 ppm MEHQ was fed to a 189 liter flash drum at the base of a 32 tray distillation column at 235 pounds per hour. The MMA was refluxed up the column at approximately 500 mm Hg vacuum. An inhibitor stream containing 5% PTZ and 2.5% MEHQ in MMA was fed into the top of the column at 1 pound per hour. HEOX was fed to the distillation column at the 28$^{th}$ tray from the base at 160 pounds per hour. Methanolic magnesium methylate (8%) catalyst was fed to the 20$^{th}$ tray from the base of the column at 43 pounds per hour. Trays between the 28$^{th}$ tray from the base and the 20$^{th}$ tray from the base were used to azeotropically dehydrate water from the HEOX. The refluxing MMA azeotropically carried the methanol coproduct to the top of the column, driving the reaction forward. The reflux ratio was adjusted to give a head temperature of from 66 to 72° C. Steam pressure on the reboiler at the base of the column was adjusted to from 115 to 117° C. After an hour, 6$^{th}$ plate analysis showed 74% MMA, 27% OXEMA, and less than 1% HEOX. The column overheads comprising MMA, methanol, and water azeotropes were collected for recovery of the MMA. The column bottoms were continuously stripped and the MMA overheads recycled to the base of the column. The stripped bottoms were then continuously rectified to give 230 pounds per hour of 95% pure OXEMA.

Example 13 - 2-Isopropyl-3-hydroxyethyl-oxazolidine Bis-ester

**[0033]** To a 2-liter round bottom, four neck flask equipped with a thermocouple/temperature controller, stirrer, constant

pressure addition funnel, N2 sparge, and a reflux condenser with a straight lead distillation head was added 206.G g of 97.2% pure IPOX. The IPOX was heated to 89° C to 103° C with sparging for 2 hours. The IPOX was cooled to 35° C. Through the addition funnel, 11.5 g of 15% potassium t-butoxide in t-butanol was added with stirring. The stirred flask was heated to 92.5° C over 16 minutes. To the heated solution was added 100.2 g of mixed DBE dropwise over 30 minutes at a temperature range of from 91.1 to 94.7° C. The stirred reactor was held at from 91.1 to 94.9° C under 137 to 210 mm Hg for 90 minutes. The batch was analyzed. paralysis indicated 97.2% IPOX and 2.7% high molecular weight impurities. The batch was stirred for 20 minutes at 94.9 to 95.5° C and 139 mm Hg. The batch was cooled to 80° C and 5.8 g of 15% potassium t-butoxide in t-butanol was added. The reactor was heated at 91.4 to 97.4° C under 96 mm Hg for 1 hour. Analysis showed 74.1% bis ester of IPOX, 11.2% half ester of IPOX, 12.2% IPOX, and 2.5% high molecular weight impurities. The stirred reactor was heated at 94.4 to 97.4° C at 96 mm Hg for another hour. Analysis showed 77.1% bis ester of IPOX, 9.4% half ester of IPOX, 11.1% IPOX, and 2.4% high molecular weight impurities. The batch was cooled to 60° C over 45 minutes. To the batch was added 163.1 g heptane, followed by 71.6 g water and 2.4 g sulfuric acid. The entire mixture was then transferred to a separatory funnel and allowed to stand overnight. The aqueous layer was drained off. The organic layer was returned to the flask, and the heptane was stripped off at 700 mm Hg and 60 to 84° C over 2 hours. Analysis of the final product showed 76.5% bis ester of IPOX, 10.7% half ester of IPOX, 8.5% IPOX, and 3.5% high molecular weight impurities.

Example 14 - Preparation of 4-Methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical

**[0034]** A mixture of 250.3 grams (2.5 moles) of methyl methacrylate (MMA), 0.4 grams (0.00323 moles) of MEHQ and 86.85 grams (0.0.504 moles) of 4-hydroxy-2,2,6,6-tetramethyl piperidinyl free radical ("4-hydroxy TEMPO") were added to a 1 liter 4-necked flask equipped with a thermocouple with temperature readout, mechanical stirrer and a 1 inch (2.54 cm) diameter 10 plate Oldershaw column fitted with a distillation head, distillate rate removal-vapor pressure temperature controller, and a graduated distillate receiver. The mixture was stirred and heated to reflux under reduced pressure (700 mm of Hg) for 0.5 hours while removing the MMA-water azeotrope. During the dehydration stage of the batch the temperature at the top of the column was 86.9 to 97.3°C and the temperature in the pot was 104°C. At the conclusion of the dehydration of the batch 5.65 grams (0.01 mole) of tetraethylhexyl titanate was added. The mixture was stirred and heated to reflux under reduced pressure (700 mm of Hg) for 2 hours. while removing the MMA-methanol of reaction azeotrope. The progress of the reaction was monitored by refractive index analysis of the MMA-methanol of reaction distillate. During the reaction stage of the batch the temperature at the top of the column was 63.9 to 99.7°C and the temperature in the pot was 98 to 108°C. The conversion of 4-hydroxy-TEMPO to 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical ("4-HT methacrylate") was calculated to be 96.8 % based on the methanol of reaction - MMA azeotrope removal and its analysis for methanol content by refractive index. The reaction mixture was allowed to stand at ambient temperature overnight and the suspension formed was decanted. The crystalline solid was air dried to yield a first crop of 6.54 grams of 4-HT methacrylate. The MMA was removed from the filtrate on a rotary evaporator and the solid residue was washed with heptane and air dried to yield a second crop of 33.2 grams of 4-HT methacrylate. According to quantitative high-performance liquid chromatography (HPLC) the heptane washed and dried solid contained 99.2 % 4-HT methacrylate. The melting point of the product was 85-86.5 °C.

Example 15 - Preparation of 4-Hydroxy-2,6,6-tetramethyl N-hydroxy piperidine

**[0035]** To a stirred solution of 126.52 grams (0.735 moles) of 4-hydroxy-2,2,6.6-tetramethyl piperidinyl free radical in 632.64 grams (6.32 moles) of methyl methacrylate was added 65.4 grams (0.73 moles) of N,N-diethyl hydroxylamine. The mixture was stirred at ambient temperature for approximately 5 hrs. and allowed to stand at ambient temperature overnight. The suspension was vacuum filtered. The filter cake was washed with MMA and air dried to yield 88.06 grams of 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine. The melting point of this product was 55-157 °C.

Example 16 - Inhibitor Effectiveness

**[0036]** A Base Stock of 660 g of the monomer composition from Example 8, 0.167 mole % (standard amount) DBTO as catalyst and 60.6 ppm (0.2x standard amount) of 4-hydroxy TEMPO as inhibitor was prepared. Four 100 ml one-neck boiling flasks were each set up with a magnetic stir bar and fitted with Y adapter, pot thermometer, West condenser, and heating mantle controlled by a rheostat (set at 65 volts) plugged into a Thermowatch temperature control device. Each flask was charged with a 40 g mixture as follows:

| | |
|---|---|
| Flask # 1 | Base Stock |
| Flask # 2 (Comparative) | Base Stock with an extra 300 ppm 4-hydroxy TEMPO added. |

(continued)

| | |
|---|---|
| Flask # 3 | Base Stock with 300 ppm 4-HT methacrylate added. |
| Flask # 4 | Base Stock with 300 ppm 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine added. |

**[0037]** All of the above samples were maintained at 92-95°C with agitation and were open to the atmosphere. All samples ran continuously (overnight) at the conditions stated during weekdays, but were cooled to room temperature for the weekend. Samples were tested for soluble polymer by methanol and butyl acrylate ("BA") dilution tests at least twice a day. Methanol and BA dilution tests were conducted using a 1:10 ratio of sample to diluent. The samples passed the soluble polymer tests if a clear solution was obtained. The samples failed the soluble polymer tests if haziness or cloudiness was observed. These results are reported below.

| Dilution Test | Flask | Time to Fail (hours) |
|---|---|---|
| Methanol | 1 | 24 |
| | 2 | 164 |
| | 3 | 132 |
| | 4 | 132 |
| BA | 1 | 24 |
| | 2 | 157 |
| | 3 | 132 |
| | 4 | 115.5 |

**[0038]** The above data clearly show that 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical and 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine are effective inhibitors of unwanted monomer polymerization.

## Claims

1. A process comprising:

a) forming a reaction mixture by admixing:

1) an alcohol selected from the group consisting of hydroxyethyl ethylene urea, ethoxylated cetyl-stearyl alcohol, ethoxylated lauryl-myristyl alcohol, dicyclopentenyloxyethyl alcohol, and hydroxyethyl oxazolidine;
2) from 10 to 10,000 parts per million based on the alcohol charge of at least one inhibitor selected from the group consisting of diethylhydroxylamine, p-methoxy phenol, hydroquinone, phenothiazine, 4-hydroxy-2,2,6,6-tetramethyl piperidnyl free radical, 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical, and 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine;
3) methyl methacrylate, wherein the mole ratio of alcohol to methyl methacrylate is from 1:1 to 1:20; and
4) from 0.1 to 10 mole percent of a catalyst selected from the group consisting of dibutyl tin oxide, reaction products of dibutyl tin oxide with components in the transesterification of various alcohols with alkyl (meth) acrylates; dibutyl tin dimethoxide, reaction products of dibutyl tin dimethoxide with components in the transesterification of various alcohols with alkyl (meth)acrylates; methanolic magnesium methylate; lithium, lithium carbonate, and lithium hydroxide;

b) reacting the alcohol with the methyl methacrylate at a temperature of from 60 to 140°C and a pressure of from 400 mm Hg to 760 mm Hg;
c) creating a crude product by azeotropically removing a mixture of methyl methacrylate and methanol;
d) optionally adding water to enable recycling of the catalyst;
e) optionally recycling the methyl methacrylate; and
f) optionally distilling the crude product.

2. A process according to claim 1 wherein:

a) the amount of the inhibitor is from 100 to 5,000 parts per million based on the alcohol charge;
b) the mole ratio of alcohol to methyl methacrylate is from 1:1 to 1:15;
c) the amount of the catalyst is from 0.5 to 7 mole percent; and
d) the reaction is run at a temperature of from 70-125°C.

3. A process according to claim 1 wherein:

a) the amount of the inhibitor is from 200 to 3,000 parts per million based on the alcohol charge;
b) the mole ratio of alcohol to methyl methacrylate is from 1:1.2 to 1:10;
c) the amount of the catalyst is from 1 to 5 mole percent; and
d) the reaction is run at a temperature of from 100-120°C.

4. A process according to claim 3 wherein the catalyst is lithium hydroxide.

5. A compound selected from the group consisting of 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical and 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine.

6. A composition comprising at least one monomer selected from the group consisting of N-(2-methacryloyloxyethyl) ethylene urea, ethoxylated cetyl-stearyl methacrylate, ethoxylated lauryl-myristyl methacrylate, dicyclopentenyloxyethyl methacrylate, and oxazolidinylethyl methacrylate and at least one compound selected from the group consisting of 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical and 4-hydroxy-9,6,6-tetramethyl N-hydroxy piperidine.

7. A method of inhibiting the unwanted polymerization of a monomer comprising combining with said monomer at least one compound selected from the group consisting of 4-methacryloyloxy-2,6,6-tetramethyl piperidinyl free radical and 4-hydroxy-2,6,6-tetramethyl N-hydroxy piperidine.

8. An inhibited monomer composition prepared according to the process of claim 1.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 98 30 6833

## DOCUMENTS CONSIDERED TO BE RELEVANT

| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
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